CERTIFICATE

- I, Futoshi HAYAKAWA, c/o KYORITSU INTERNATIONAL, 3-2-5 Meieki, Nakamura-ku, Nagoya-shi, Aichi-ken, Japan, hereby solemnly and sincerely declare:
- (1) THAT I am well acquainted with the Japanese language and English language, and
- (2) THAT the attached translation is a true and accurate translation into the English language of the official copy of the document in respect of an application for a Japanese Unexamined Patent Publication No. 10-088361 published in Japan on the 7th day of April 1998, and of the official certificate attached thereto.

Futoshi HAYAKAWA

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PATENT ABSTRACTS OF JAPAN

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(21)Application number: 08-245367 (71)Applicant: FURUKAWA ELECTRIC

CO LTD

(22)Date of filing: 18.09.1996 (72)Inventor: ASAKURA TOYOMITSU

HONDA FUMIHIRO

[Title of the Invention]

Method of electroless-plating a polymer molded body

[Abstract]

- 5 [Object] An object of the present invention is to provide a method of electroless-plating a polymer molded body to obtain a plating layer having high adhesion and high decorativeness without using dangerous and pollution-inducible chemicals.
- [Means for Accomplishing the Object] Surface treatment is performed as the pretreatment for electroless-plating a polymer molded body. The surface treatment comprises: irradiating a predetermined region of the polymer molded body with ultraviolet (UV); and bringing the region into contact with an alkaline solution containing a nonionic surfactant having a polyoxyethylene bond (- (OCH₂CH₂)_{n-}).

[Claims]

[Claim 1]

A method of electroless plating a polymer contact, in which Surface treatment is performed as pretreatment for electroless-plating a polymer molded body, the surface treatment comprising irradiating a predetermined region of the polymer molded body with ultraviolet (UV); and bringing the region into contact with an alkaline solution containing

a nonionic surfactant having a polyoxyethylene bond (- $(OCH_2CH_2)_{n-}$).

[Claim 2]

The method of electroless plating a polymer contact according to claim 1, wherein the polymer molded body is an impact-resistant polystyrene resin or an acrylonitrile butadiene styrene (ABS) resin.

[Detailed Description of the Invention]

10 [0001]

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[Technical Field] The present invention relates to an electroless plating method for forming a plating layer having high adhesion and high decorativeness on the surface of a polymer molded body.

15 [0002]

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[Background Art] When a copper or nickel plating layer is formed on a polymer molded body, such as film, sheet, fiber, resin molded products, made of a polymer material, before plating the polymer molded body, the surface treatment of the polymer molded body is generally performed. Due to this surface treatment, a functional group is imparted to the surface of the polymer molded body, recesses and protrusions are formed on the surface of the polymer molded body, and the adhesion of a plating layer can be obtained by a chemical bond between the surface of the polymer molded body

and the plating layer and an anchor effect.

As an example of the surface treatment, there is a process of immersing the polymer molded body into a chemical, such as a mixture of chromic acid and sulfuric acid, a 5 mixture of dichromic acid and sulfuric acid, chloric acid, a mixture of sulfuric acid and perchloric acid, or the like. For example, an acrylonitrile butadiene styrene (ABS) resin, which accounts for a large percentage of electroless-plated plastic, is surface-treated using a mixture of chromic acid and sulfuric acid. However, this method is problematic as 10 Dangerous and pollution-inducible chemicals are used. It is difficult to selectively surface-treat a predetermined region of a polymer molded body, with the result that even an unnecessary region of the polymer molded body is plated. Since mirror surface plating is performed 15 in order to form recesses and protrusions on the surface of the polymer molded body, it is required that the polymer molded body is thickly plated. Further, even though the surface of the polymer molded body becomes mirror surface (gloss surface) by thickly plating the polymer molded body, 20 recesses and protrusions remain on the plated surface of the polymer molded body, so that a mirrored image is distorted, with the result that high decorativeness cannot be obtained. [0004]

25 [Problems to be Solved by the Invention] An object of the

present invention is to provide a method of electrolessplating a polymer molded body, by which the above problem can be solved, and a plating layer having high adhesion and high decorativeness can be obtained without using dangerous and pollution-inducible chemicals.

[0005]

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[Means for Solving the Problems] The present inventors have keenly examined surface treatment methods through UVirradiation as surface treatment without using dangerous and 10 pollution-inducible chemicals, and, as a result, they found that а plating layer having high adhesion and decorativeness can be formed by continuously performing UVirradiation. Based on this finding, the present invention was completed.

15 [0006] In order to accomplish the above object, the present invention provides a method of electroless plating a polymer contact, in which surface treatment is performed as pretreatment for electroless-plating a polymer molded body, the surface treatment comprising irradiating a predetermined 20 region of the polymer molded body with ultraviolet (UV); and bringing the region into contact with an alkaline solution containing a nonionic surfactant having a polyoxyethylene bond (- $(OCH_2CH_2)_{n-}$).

[0007]

25 [Embodiments] In the present invention, as the pretreatment

for electroless-plating the surface of a polymer molded body, the polymer molded body is irradiated with UV and is then treated with an alkaline solution (that is, the polymer molded body is brought into contact with an alkaline solution). As the alkaline solution, an alkaline solution containing a nonionic surfactant having a polyoxyethylene bond (- $(OCH_2CH_2)_{n-}$) may be used.

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The wavelength region of ultraviolet applied to the polymer molded body may be suitably selected in a range of 200 ~ 400 nm although it depends on the material of the polymer molded body. The polymer molded body is irradiated with a UV of proper wavelength, so that a part of the chemical bond of the polymer molded body is cut to form a radical, with the result that the radical is combined with oxygen to oxidize and degrade the surface of the polymer molded body, thereby imparting a functional group to the polymer molded body. The amount of the irradiated ultraviolet is required to be suitably selected depending on the material of the polymer molded body such that surface treatment effect can be obtained. For example, in the case of polystyrene resin, а an ABS resin, or polymethylmethacrylate resin, the UV-irradiation thereof may be performed on condition that a deuterium lamp of 30W, having a radiation wavelength of $160 \sim 400$ nm, is used, the irradiation distance thereof is 25 mm, and the irradiation

time thereof is about 300~1000 seconds.

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[0009] In the present invention, the material of the polymer molded body, which is a subject to be plated, is not particularly limited as long as the surface thereof is chemically changed by oxidation reaction due to UV-irradiation. Examples of the material of the polymer molded body may include an impact-resistant polystyrene (HIPS) resin, an acrylonitrile butadiene styrene (ABS) resin, a polymethylmethacrylate (PMMA) resin, a polyamide resin, a polyester resin, an epoxy resin, and the like.

[0010] Prior to the UV-irradiation, the surface of the polymer molded body, which is a subject to be surface-treated, is made clean using conventional washing treatment including, for example, degreasing and water washing, and the like. Due to this washing treatment, the surface treatment effect of the polymer molded body is effectively exhibited.

[0011] In the alkaline solution treatment, which is subsequent to the UV-irradiation, an alkaline solution containing a nonionic surfactant having a polyoxyethylene bond (- $(OCH_2CH_2)_n$ -) is used. As the nonionic surfactant, polyoxyethylene alkyl ether and polyoxyethylene aliphatic acid monoester may be used. Typical examples of the nonionic surfactant may include polyoxyethylene lauryl ether and polyoxyethylene sorbitan monostearate. It is preferred

that the of the nonionic surfactant having a amount polyoxyethylene (POE) bond in the alkaline solution be $0.05 \sim 1g/liter$. When the amount of the nonionic surfactant is present in the above range, a plating layer having improved adhesion can be obtained, thus which is preferable. Further, sorbitan aliphatic acid ester having no polyoxyethylene (POE) bond, although it is a nonionic surfactant, does not contribute to the improvement of adhesion of a plating layer of the present invention. when cationic surfactants or anionic surfactants are used, the adhesion of a plating layer of the present invention is not imporoved.

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[0013] The alkaline component in the alkaline solution is not particularly limited. As the alkaline component, sodium hydroxide (NaOH), sodium carbonate (NaCO₃), ammonia (NH₃), tribasic sodium phosphate (Na₅P₃O₁₀), or the like may be used. It is preferred that the concentration of the alkaline solution be about $0.05\sim0.5$ mol/liter. The alkaline solution treatment may be suitably and selectively performed at an alkaline solution temperature of $30\sim80\%$ for $30\sim5$ seconds.

[0014] After the surface treatment, the polymer molded body is washed with water, and is then provided in an electroless plating treatment process. The electroless plating treatment may be performed using a conventional method, and may be performed by surface-catalyzing and then

acid-activating the polymer molded body, and then forming a plating layer thereon using an electroless plating solution.
[0015]

[Examples] Hereinafter, the present invention will described in detail with reference to Examples. polymer molded body, an impact-resistant polystyrene (HIPS) resin (HT500, manufactured by Idemitsu Petrochemical Co, an ABS resin (MX3, manufactured by Ltd.) and Chemical Industries, Ltd.) were injection-molded into a 10 sheet having a thickness of 3 mm using an injection molding machine. Further, a commercially available acrylic plate (PMMA) was also prepared. These sheet and acrylic plate were cut at a predetermined size, and were then degreased and washed using a mild detergent or an alkaline solution, 15 thereby preparing sample sheets for electroless plating. These sample sheets were surface-treated, were washed with water, were electroless-nickel(Ni)-plated (catalyzed → acid-activated → chemically-nickel (Ni)-plated), and then adhesion between a sheet and a plating layer 20 evaluated using the following method. Further, the electroless nickel (Ni) plating was performed using the following treatment liquids under the following treatment conditions. Further, after each of the treatment processes was completed, all of the sample sheets were washed with 25 water.

Catalyzation treatment was conducted on conditions [0016] of a treatment liquid including 0.075m3/m3 of a catalyst (A-30, manufactured by Okuno Pharmaceutical Industries, Ltd.) and 0.15m3/m3 of hydrochloric acid, a bath temperature of $30\,^{\circ}\mathrm{C}$, and an immersion time of 4 minutes. Aid activation treatment was conducted on conditions of a treatment liquid including 0.075m³/m³ of hydrochloric acid, a bath temperature of 30 $^{\circ}$ C, and an immersion time of 3 minutes. nickel (Ni) plating was conducted on conditions of a mixed solution of NiA and Nib catalyst, manufactured by Okuno Pharmaceutical Industries, Ltd., as a treatment, a bath temperature of 30° C, and an immersion time of 3° 9 minutes. The adhesion of each of the sample sheet was [0017] evaluated by further forming an electric copper (Cu) plating layer having a thickness of 15 $\mu\mathrm{m}$ on the electroless nickel plating layer formed on the sheet, attaching a cylindrical bar to the copper (Cu) plating layer using an epoxy adhesive and then cutting a plating layer formed around the cylindrical bar to prepare test pieces, measuring a toppling load (F) of the cylindrical bar by applying a load to the cylindrical bar having a diameter of 4 mm and a length of 40 mm at a load rate of 16.7 μ m/sec in a direction parallel to the plating layer, and then calculating the measured using the load (F) Equation represented by $f=4h \cdot F/\pi R^3$ (R: radius of the cylindrical bar, h: distance

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between plated surface and load point).

[0018] The washed sample sheets of Examples 1 to 5, Comparative Examples 1 to 7 and a conventional Example were surface-treated and then electroless nickel (Ni) plated on the following conditions given in Table 1, and then the external appearances of the sample sheets were observed, and simultaneously the adhesions of the sample sheets were evaluated. The results thereof are given in Table 1.

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[Table 1]

[0019]

Experimental Example	l Example	Examples	s				Compara	Comparative Examples	amples					Conventional
			2	ო	4	'n	П	2	m.	4	5	9	7	Example
Kinds of po	Kinds of polymer material	HIPS	ABS	PMMA	HIPS	ABS	HIPS	HIPS	HIPS	HIPS	HIPS	HIPS	HIPS	ABS
Surface	UV-irradiation	#d	P#	P#	#4	P#	#+ d	not	# Q.	₽# -	#4	# Q	P#	Conventional
treatment	treatment note l							P#						treatment
conditions	alkaline solution	## A	# 4	₽# -	# d	# #	# *	# - 04	## C4	#d	# -	# Q	not	note 3
	immersion				••								ъ #-	
	treatment							·						
	(2 minutes)		-				not							
	(NaOHO.lmol/liter)						## ##							
	surfactant	##	##	#		##	<u>.</u>	# #						
•	(0.1g/liter) note		Α		 							•••		
	2											•		
	1) POE								a #	<u>-</u> -				11 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1

note 1: a deuterium lamp of 30 w was used, irradiation distance of 25mm, irradiation time of 10 minutes

note 2: 1)-3) are nonionic surfactants, 4), 5) are anionic surfactant, and 6) is a cationic surfactant.

note 3: surface treatment using a mixture of chromic acid and surfuric acid (immersion at 65°C for 10 minutes) -water washing -neutralization using hydrochloric acid-surface treatment using water wahing

note 4: the surfaces of the plating layers of Examples 1 to 5 and conventional Examples are mostly formed of distorted surfaces of resin.

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* means that plating layer is not adhered or is immediately peed.

P# means "performed"; a# means "added"

From Table 1, it was found that all of the surfaces [0020] of the electroless plating sheets obtained in Examples 1 to 5 were mirrored surfaces which are not distorted, and that they have high decorativeness compared to that of a conventional Example. As shown in Table 1, it can be seen 5 that the adhesion of the eletroless plating layer obtained by performing UV-irradiation treatment and surface treatment using an alkaline solution containing a nonionic surfactant having a polyoxyethylene bond as Example 1 to 5 is equal to that of the electroless plating layer obtained by performing 10 surface treatment using a mixture of chromic acid and sulfuric acid. Further, It was found that in the case where UV-irradiation treatment is not performed, in the case where surfactant is not added in the subsequent alkaline 15 solution treatment although the UV-irradiation treatment is performed, or in the case where a surfactant having no POE bond, a cationic surfactant or an anionic surfactant is used although the surfactant is added, plating layer is not adhered on the surface of a resin.

20 [0021]

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[Advantages]

According to the electroless plating method of the present invention, as pretreatment for electroless-plating a polymer molded body, surface treatment comprising: irradiating a predetermined region of the polymer molded body with

ultraviolet (UV); and bringing the region into contact with an alkaline solution containing a nonionic surfactant having a polyoxyethylene bond is performed. Therefore, the electroless plating method of the present invention is advantageous in that a plating layer having high adhesion and high decorativeness can be obtained without using dangerous and pollution-inducible chemicals, and it is very industrially used.